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October 2018



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**October 2018**

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**<http://www.inl.gov>**

**Prepared for the  
U.S. Department of Energy  
Office of Nuclear Energy  
Under DOE Idaho Operations Office  
Contract DE-AC07-05ID14517**

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2                               **an insight into the blocking effect**

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25 **Abstract:**

26 Long-term stability of reference electrode is a major issue in lithium-ion batteries. A composite  
27 Ni-Li reference electrode (RE) with a longer lifetime than traditional Cu-wire Li reference  
28 electrodes is proposed in this study. However, the larger size of the Ni-Li RE creates a blocking  
29 effect when positioned internally in the battery. The blocking effect manifests as an abnormal  
30 feature in the measured electrode potential. A two-dimensional (2D) finite element model of the  
31 cell with an internal RE is constructed to investigate the mechanism of the blocking effect. The  
32 internal RE blocks the path of local current flow in the electrolyte, and decreases the  
33 electrochemical reaction rate of particles in the anode and cathode, leading to measurement errors.  
34 Characteristic lengths of RE and applied currents were examined as parameters in the finite  
35 element model to determine their effect on the magnitude of error. A useful guide is provided for  
36 proper selection of size of RE and applied current in dynamic tests of lithium-ion batteries.  
37

## 38 1. Introduction

39 Lithium-ion batteries are widely used in consumer electronics, electric vehicles, and energy  
40 storage, because of their high energy and power density<sup>1, 2</sup>. A RE is important in carrying out  
41 experimental tests and mechanistic investigations of lithium-ion batteries<sup>3-9</sup>. Electrode properties  
42 such as impedance or potential can be ascertained from information provided by a RE. This  
43 information enables some aging mechanisms and safety issues, such as solid electrolyte interphase  
44 (SEI) growth and such as internal short circuit<sup>10</sup> caused by lithium deposition, to be identified.

45 Although present commercial lithium-ion batteries do not have REs, most battery manufacturers  
46 are interested in monitoring the state of lithium plating with the help of a RE to improve battery  
47 safety and performance. Thus, there is a need for REs in battery research and industrial  
48 production.

49 Three categories of RE materials are used in lithium-ion batteries. The first, and most common, is  
50 lithium metal<sup>4, 5, 7-9, 11-13</sup>, which is intrinsically compatible with the non-aqueous electrolyte of the  
51 battery, provides a stable value against which the electrode potential is measured. Although the  
52 electrode potential of lithium metal is -3.04 V vs. the standard hydrogen electrode (SHE), it is  
53 customary to report potentials versus the Li/Li<sup>+</sup> value. This is convenient for post-processing  
54 experimental data. Lithium metal is also readily and reproducibly produced. The second class of  
55 RE materials includes lithium compounds, such as LiFePO<sub>4</sub> (3.4 V vs. Li/Li<sup>+</sup>) and Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> (1.5  
56 V vs. Li/Li<sup>+</sup>) etc.<sup>14</sup>, which have a known potential plateau. Lithium-containing RE must be  
57 oxidized to a specific state of charge (SOC) to provide a stable equilibrium potential. The third  
58 category of materials comprises binary lithium alloys, the most common of which is the Li-Sn  
59 alloy.<sup>3, 15, 16</sup> Li-Al<sup>17</sup>, Li-Au<sup>18</sup>, and Li-Bi<sup>6</sup> alloys also have been recommended as RE materials for

60 impedance and potential measurements. Lithium-alloy materials require a lithiation pretreatment  
61 to produce a stable reference potential. Because the lithium alloys typically exhibit more than one  
62 potential plateau, the process must be conducted carefully to produce the desired reference  
63 potential. A disadvantage of lithium compounds and alloys is reference potential drift due to  
64 lithium loss from the electrode. For this reason, we focus on lithium-metal RE materials.

65 Although REs are commonly used in potential and impedance measurements in lithium-ion  
66 batteries, some unsolved problems remain. For example, experimental distortions and artifacts are  
67 frequently observed. Jansen et al. investigated the effects of the RE size and placement and cell  
68 geometry on impedance measurements<sup>19</sup>. They concluded that a large internal RE can adversely  
69 affect impedance measurements and the misalignment of an external RE can cause errors in  
70 impedance measurements. Ender et al. evaluated the effects of geometric and electrical  
71 asymmetries using an external RE and found distortions in scaling factors and inductive artifacts  
72 in the impedance response<sup>20</sup>. Klink et al. demonstrated that geometrical asymmetry can be reduced  
73 by precise electrode alignment and use of a coaxial RE.<sup>21</sup> Delacourt et al. proposed a novel  
74 three-electrode cell set-up, in which, holes in the working and counter electrodes for RE  
75 positioning minimized distortions in the impedance spectrum.<sup>22</sup> Hoshi et al. suggested that the RE  
76 should be positioned externally between the positive and negative electrodes for optimum EIS  
77 measurements.<sup>23</sup> Ender et al. examined point-like, wire, and mesh RE designs and demonstrated  
78 theoretically and experimentally that a mesh RE best achieves distortion-free EIS measurements.<sup>8,</sup>  
79 <sup>24</sup> Although EIS measurements with a RE have been investigated extensively, only a few studies  
80 have examined the effects of RE placement and design in dynamic tests of lithium-ion batteries,  
81 which are important in investigating the fast charge<sup>11, 25</sup> and aging mechanism.<sup>4, 7, 26, 27</sup> Klett et al.

82 compared positive and negative electrode potentials measured simultaneously with internal and  
83 external REs during a 10 s, 3 C pulse charge, and found that the internal RE is more accurate.<sup>16</sup>  
84 However, poor long-term stability of REs is a major issue, particularly in investigations of  
85 capacity fade. Designs based on Li-plating onto a Cu wire exhibit potential drift shortly after  
86 production, because the small amount of lithium is easily dissolved or consumed by SEI growth.  
87 Lithium alloys, which exhibit multiple potential plateaus, presumably suffer from potential drift  
88 when the intercalation state is unexpectedly altered.<sup>15</sup> This also occurs with lithium compounds.  
89 Therefore, lithium metal remains the most suitable RE material for lithium-ion batteries, despite  
90 its possible depletion in the electrolyte.  
91 In summary, an internal lithium RE, which provides more accurate electrode potential  
92 measurement, is preferred for dynamic testing, although a small size is needed to reduce blocking  
93 effects. However, the amount of active lithium must be as large as possible to extend electrode  
94 lifetime. The trade-off between measurement accuracy and lifetime is a limiting factor in the  
95 application of Cu-wire based lithium REs.  
96 In this study, a new RE design with a greater active lithium loading is proposed and compared in  
97 terms of performance with the Cu-wire-Li RE. The blocking effect of an internally positioned RE  
98 also is investigated under dynamic conditions based on experimental measurements and a 2D  
99 electrochemical model. Quantitative analysis of the blocking effect provides a general guide for  
100 selecting the proper characteristic length of RE and range of applied current.

## 101 **2. Experiment and model description**

### 102 **2.1 Reference electrode setup**

103 Two reference electrode setups were compared to evaluate the effect of RE geometry on electrode

104 potential measurements in dynamic battery tests.

105 Lithium metal deposited onto a Cu wire substrate was used for Setup 1. The diameter of the Cu  
106 wire was 25  $\mu\text{m}$ , which approximates the dimension of the separator. One tip of a 2-cm-long Cu  
107 wire was immersed in dilute sulfuric acid and washed thoroughly with stirring in water and  
108 ethanol. This process produced a Cu wire with a polished tip ready for lithium deposit. The  
109 polished tip was inserted carefully into the jelly roll between positive and negative electrodes. The  
110 inserted portion of Cu wire was covered by a separator to avoid an internal short circuit. After  
111 assembly, a 20- $\mu\text{A}$  direct current was passed between the Cu wire and positive electrode and Cu  
112 wire and negative electrode successively for 1 h to form a uniform lithium deposit.<sup>28</sup> This  
113 completes production of the Cu-wire-Li RE.

114 Lithium metal applied to a Ni-foam substrate was used for Setup 2. The larger size of the Ni foam  
115 (ca. 0.1-mm thick  $\times$  1-mm wide) provided greater lithium loading. As described by Cui et al.<sup>29</sup> and  
116 Zhang et al.<sup>30</sup>, a piece of Ni foam was immersed into molten lithium, which formed a composite  
117 RE by infusion of Li into the Ni host. One side of the RE was attached to a Ni current collector by  
118 ultrasonic welding.

119 Subsequent experiments demonstrated that RE reliability and lifetime were greater with Setup 2.  
120 Because lithium is consumed during use, a greater amount of lithium leads to a longer RE  
121 lifetime<sup>6,28</sup>. The superior performance of Setup 2 is attributed to its greater lithium loading, which  
122 unavoidably introduces blocking effects due to RE size.

## 123 **2.2 Experiment**

124 Two commercial  $\text{LiNi}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2}\text{O}_2$  (NCM)/graphite batteries with nominal capacities of 40 Ah  
125 for Cell A and 24 Ah for Cell B were selected for experimentation. Set-up 1 was applied to Cell A

126 and Set-up 2 to Cell B. Setup 1 was applied to Cell A. Setup 2 was applied to Cell B. Cells A and  
127 B were large enough to neglect the impact of the RE on the cell terminal voltage. However, there  
128 was a difference in the time of RE emplacement. The Cu wire in Setup 1 was inserted into the  
129 jelly roll before the cell was sealed with the help of the manufacturer. In Setup 2, Cell B was  
130 discharged to 2.5 V and transferred to a dry room with a dewpoint of -70 °C. The Al-plastic film  
131 of Cell B was carefully cut open and partially peeled away to leave enough space to separate the  
132 positive and negative electrodes and insert the Li-Ni RE, which was wrapped with an additional  
133 piece of separator to inhibit short-circuiting. The cell was resealed using a new Al-plastic film  
134 with the Li-Ni RE positioned between the positive and negative electrodes.

135 It is worth mentioning that one-terminal and two-terminal configurations were typically used for  
136 application of REs. Although there is no issue of inconsistency in the one-terminal configuration,  
137 there is an undesirable interaction with the measuring circuit when the anode and cathode are  
138 monitored simultaneously. The effect is suppressed in the two-terminal configuration, but either  
139 format is feasible for electrode potential measurements. In this study, we adopt the one-terminal  
140 configuration, because it is sufficient to investigate the blocking effect of the RE.

141 A series of dynamic tests were performed on Cells A and B after the REs were implanted to  
142 examine the impact of RE size on electrode potential measurements.

143 1) Capacity test: Cells were charged with a constant current-constant voltage (CC-CV) protocol  
144 until the upper cut-off voltage and cut-off current were reached. This was followed by a constant  
145 current (CC) discharge to a lower cut-off voltage. A rest period was observed between charging  
146 and discharging. Three cycles were conducted to evaluate the reproducibility of the voltage  
147 measurement. The voltage ranges of Cells A and B were 4.2–2.8 V and 4.2–2.5 V, respectively.

148 The currents applied for charging and discharging, as suggested by the manufacturers, were 1 and  
149 1/3 C for Cells A and B, respectively. The cut-off current was preset at 0.05 C for both cells.

150 2) C-rate test: Cells were charged at C-rates of 0.2, 0.5, and 1 C. The C-rates of discharge  
151 suggested by the manufacturers were 1 and 1/3 C for Cells A and B, respectively. A 2 h rest period  
152 was applied between charging and discharging to allow the cells to regain equilibrium.

153 3) RE test: This test was designed to compare different ranges of SOC operation. Two discharge  
154 protocols with differently terminated SOC were performed with Cell B. The cell was first  
155 discharged at a rate of 1/3 C from 0.03 to 0 SOC followed by a 1h rest period. The cell was then  
156 charged to 0.5 SOC at a rate of 1/2 C followed by a 3 h rest period. Finally, the cell was  
157 discharged at a rate of 1/3 C from 0.5 to 0.2 SOC followed by a 3 h rest period.

158 All tests were performed on an 8-channel Neware BTS 4000 test station. The electrode potential  
159 was measured with a 6 ½-digit multimeter (Keithley 2000) with an input impedance of >10 GΩ.

160 The high input resistance reduces the leakage current to 100 pA or less, which improves  
161 measurement accuracy and minimizes consumption of the reference electrode. The digital  
162 multimeter was used in combination with a 10-channel scanner (Keithley 2000-SCAN), which  
163 enabled simultaneous measurement of the anode and cathode potentials. The positive input of the  
164 multimeter was connected to the current collector of the negative/positive electrode, and the  
165 negative input was connected to the current collector of the reference electrode.

### 166 **2.3 Finite element model (FEM)**

167 A 2D FEM was built to investigate battery behavior with an internal RE. Fig. 1 shows the  
168 schematic shows a schematic of the 2D FEM geometry for simulation. Characteristic widths and  
169 thicknesses are considered in the model, which neglects the deformation of the separator and

170 electrode caused by implanting the RE.

171 The electrochemical model is configured to a 2D description of the cell dynamics. Apart from the  
172 presence of the RE, the model is based on the work of J. Newman et al.<sup>31</sup> Charge and mass  
173 conservations are formulated by different partial differential equations (PDE) in the solid and  
174 electrolyte phases with corresponding boundary and initial conditions and coupled with a kinetic  
175 equation to describe the relationship between the overpotential and the lithium exchange flux (i.e.,  
176 a Butler-Volmer equation). The principal equations are introduced here without their boundary and  
177 initial conditions.

178 Mass conservation in solid phase is given by:

$$\frac{\partial c_s}{\partial t} = \frac{D_s}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial c_s}{\partial r} \right) \quad (1)$$

179 where  $D_s$  is the solid phase diffusion coefficient. Mass conservation in the electrolyte phase is  
180 given by:

$$\frac{\partial}{\partial t} \varepsilon_e^j c_e = \nabla \left( D_{e,\text{eff}}^j \nabla c_e \right) + a_s (1 - t_+) j, \quad j = \text{n,p} \quad (2)$$

$$\frac{\partial}{\partial t} \varepsilon_e^s c_e = \nabla \left( D_{e,\text{eff}}^s \nabla c_e \right) \quad (3)$$

181 where  $\varepsilon_e$  is the volume fraction of electrolyte, and  $D_{e,\text{eff}}$  is the effective electrolyte diffusion  
182 coefficient. Eq. (2) is used in the negative and positive electrode regions, while Eq. (3) is used in  
183 the separator region. The lithium exchange flux,  $j$ , equals zero in the separator region. Charge  
184 conservation in the solid phase is:

$$\nabla \left( \sigma_{\text{eff}} \nabla \phi_s \right) - a_s F j = 0 \quad (4)$$

185 where  $\sigma_{\text{eff}}$  is the effective electrical conductivity in the solid phase. Charge conservation in the  
 186 electrolyte phase is:

$$\nabla(\kappa_{\text{eff}} \nabla \phi_e) + \nabla \left( \frac{2RT(t_+^0 - 1)\kappa_{\text{eff}}}{F} \left( 1 + \frac{\partial \ln f_{\pm}}{\partial \ln c_e} \right) \nabla \ln c_e \right) + a_s F j = 0 \quad (5)$$

187 where  $\kappa_{\text{eff}}$  is the effective electrical conductivity in the electrolyte phase. The kinetic equation has  
 188 the form:

$$j = k_0 c_e^{1-\alpha} (c_{s,\text{max}} - c_{s,e})^{1-\alpha} c_{s,e}^{\alpha} \left( \exp\left(\frac{(1-\alpha)F}{RT} \eta\right) - \exp\left(\frac{-\alpha F}{RT} \eta\right) \right) \quad (6)$$

$$\eta = \phi_s - \phi_e - U_{\text{eq}} - FR_{\text{SEI}} j \quad (7)$$

189 where  $k_0$  is reaction rate constant. The overpotential,  $\eta$ , is defined in Eq. (7), where  $U_{\text{eq}}$  is the  
 190 equilibrium potential for the charge transfer reaction.

191 The rectangular RE is positioned between the two electrodes as shown in Fig. 2. Lithium  
 192 exchange occurs only on the surface of the RE. Therefore, the charge conservation in the RE  
 193 region is:

$$\nabla(\sigma^{\text{RE}} \nabla \phi_s) = 0 \quad (8)$$

194 where  $\sigma^{\text{RE}}$  denotes the electrical conductivity of the RE (lithium metal). The electrode potential  
 195 measured versus the solid phase potential of the RE is given by:

$$\phi_s^{\text{RE}} = \phi_e + U_{\text{eq}}^{\text{RE}} \quad (9)$$

196 where the equilibrium of the RE is equals zero. This equation is applied on a presentative point on  
 197 the surface of the RE and simulated electrode potential is equal to the difference between the solid  
 198 potential of the electrode and the RE. All the simulations were carried out in Comsol  
 199 Multiphysics.

## 200 **3. Results and Discussion**

### 201 **3.1 Abnormal feature(s) of the electrode potential**

202 To determine if overall battery performance is affected by the presence of an internal RE, cell  
203 capacities were compared with and without the RE. For Setup A, the cell capacity of 40.39 Ah  
204 without the RE changed to 39.89 Ah after the RE was implanted. For Setup B, the cell capacity  
205 was 25.10 and 25.01 Ah before and after RE implantation, respectively. The internal RE appears to  
206 have little impact on the battery performance. The anode potential in Setup A was always greater  
207 than 0 V during the C-rate test, whereas the anode potential in Setup B decreased to 0 V at 0.5 and  
208 1 C. The electrode potential profiles in Setup B also exhibited an abnormal feature compared with  
209 Setup A. Fig. 3 illustrates the characteristics of the abnormal feature by comparing electrode  
210 potential profiles for Setups A and B during rest periods in the C-rate tests. For Setup A, a  
211 continuous decrease is observed in the cathode or anode potential during the rest period, which is  
212 attributed to a depolarization. However, this behavior is not observed with Setup B. The at-rest  
213 anode potential after cell discharge first decreases for ca. 1 h, but is followed immediately by a  
214 curious increase. Similar behavior also occurs after a rapid initial decrease in the at-rest cathode  
215 potential following cell charging. These observations contrast distinctly with the anticipated  
216 depolarization behavior of an electrode according to the electrochemical battery model.

217 The abnormal change in voltage that appears reproducibly in the dynamic experiments is  
218 considered to be a genuine feature rather than an experimental artifact. The presence of the feature  
219 demonstrates that an internal RE produces pronounced differences in electrode potential behavior  
220 during dynamic tests of lithium-ion batteries. Differences in the excitation time and time constant  
221 are observed between the cathode and anode potential responses, which suggest that the feature is

222 governed by electrode architecture and material properties. The defining characteristic of the  
223 abnormal feature is the anomalous increase in anode/cathode potential during the rest period  
224 following cell discharge/charge rather than a continuous decrease until an equilibrium state is  
225 reached. A schematic depiction that highlights the abnormal feature is presented in Fig. 4 (b) with  
226 the abnormal increase highlighted. Fig. 4 (a), displays the normal response for comparison.

### 227 **3.2 Model fitting**

228 Specifically designed RE dynamic experiments were conducted to examine the origin,  
229 characteristics, and mechanism of the abnormal feature. The anode potential was the first  
230 parameter investigated. A short-term discharge was conducted to see if operation time was a factor.  
231 Cell B was allowed to rest for 3 h to ensure full relaxation and then discharged as shown in Fig. 5  
232 (a) with a current of  $1/3$  C from an initial voltage of 3.265 V to a cut-off voltage of 2.500 V for  
233 264 s followed by a rest period of 1 h. The anode potential in Fig. 5 (b) increases initially from  
234 0.387 to 0.501 V until the end of discharge and then decreases to 0.473 V over the next 60 s  
235 followed by an increase to 0.553 V at the end of the rest period. This confirms that the abnormal  
236 feature is present even after a short period of operation.

237 A second experiment was conducted to examine the effect of the SOC on the abnormal feature,  
238 because the cell had been discharged to 0 SOC in all previous experiments. Cell B was adjusted to  
239 0.5 SOC by first discharging to 0 SOC and then recharging at 1 C for 30 min followed by a 3 h  
240 rest period. The cell was then discharged from 0.5 to 0.2 SOC at  $1/3$  C for 0.86 h followed by  
241 another 3 h rest period as shown in Fig. 6. The anode potential increases from 0.147 to 0.219 V  
242 during discharge and then decreases to 0.207 V over 380 s before reversing and increasing slightly  
243 to 0.209 V during the rest period. The behavior of the abnormal feature is much less pronounced

244 in the second experiment, wherein the potential increment is 0.002 V rather than 0.080 V. This  
245 difference may result from operation over different SOC ranges, which will be elaborated upon in  
246 the next section.

### 247 **3.3 An explanation of the abnormal feature: blocking effect**

248 Very little discussion was found in the literature on the behavior we have observed, because  
249 electrode potential data, which have been measured with different REs, have not been closely  
250 examined during rest periods. The origin of the abnormal feature is explored in this section. There  
251 are two likely sources of the difference in electrode potential behavior between Setup A and Setup  
252 B.

253 The first possible cause is the RE itself, which suggests that its potential may deviate from the  
254 standard value. In this case, undesirable reactions may occur at the interface between the Li metal  
255 and electrolyte leading to SEI film formation. When the RE is immersed in the electrolyte,  
256 parasitic reactions between metal and electrolyte species occur immediately and form compact,  
257 insoluble products on the RE<sup>32</sup>. These reactions may alter the RE potential. However, the  
258 behavior of Li as a RE differs from that as an anode. Very little current is applied to the RE,  
259 because of the high input impedance of the voltmeter. Therefore, reactions between Li and the  
260 electrolyte should be minimal. The difference in time constant between the anode and cathode  
261 potential response indicates that the abnormal feature is not related to the RE, because this  
262 parameter should be similar in both cases.

263 A second possible cause is the blocking effect of the RE, which has not been considered in  
264 equilibrium EIS measurements.<sup>23,33</sup> The proposed 2D electrochemical model provides insight into  
265 the blocking effect of the RE and a quantitative discussion of errors during dynamic

266 measurements.

267 Electrolyte concentration distribution around the RE during a 3200 s discharge followed by a 1800  
268 s rest period is demonstrated in Fig. 7, where the anode, separator, and cathode are shown from  
269 left to right. Lithium ion transport from one electrode to another is blocked by the RE, which acts  
270 as a physical barrier and increases the electrolyte concentration on the anode side and decreases  
271 that on the cathode side. The maximum difference between the electrolyte concentration in the  
272 blocked area and that at the same x-axis coordinate in the unblocked area,  $(\Delta C_e)_{\max}$ , increases with  
273 time. The difference increases to about 1700 mol/m<sup>3</sup> at 3000 s and decreases to about 417 mol/m<sup>3</sup>  
274 at 5000 s. The blocked area extends about 0.2 mm beyond the edge of the RE, which has a width  
275 of 0.4 mm.

276 The average solid-phase composition of the anode during discharge is shown in Fig. 8. Anode  
277 particles in the blocked area have greater solid-phase concentration than those in the unblocked  
278 area. Consequently, lithium deintercalation of particles in the blocked area is driven primarily by  
279 the solid-phase concentration gradient, which impedes the flow of current between the two  
280 electrodes. However, unlike the electrolyte, the maximum difference in solid-phase concentration  
281 between the blocked and unblocked regions at the same x-axis displacement,  $(\Delta C_{s,\text{avg}})_{\max}$ , does not  
282 increase.  $(\Delta C_e)_{\max}$  equals 3267, 4169, and 3755 mol/m<sup>3</sup>, respectively, at 1000s 2000 s and 3000 s.

283 During the rest period after 3200 s,  $(\Delta C_e)_{\max}$  decreases gradually with time to reach an equilibrium  
284 state, which indicates that the solid-phase lithium in the blocked area diffuses across the  
285 concentration gradient to the particles in the remaining area. This is not strictly a physical  
286 diffusional process, in which the electrolyte bridges between different particles, because the bulk  
287 solid-phase potential is nearly uniform over the entire region of the electrode. Thus, the abnormal

288 potential relaxation behavior results from the difference in electrolyte potential adjacent to and  
289 remote from the RE.

290 The internally positioned RE not only blocks  $\text{Li}^+$  transport in the electrolyte phase, but also  
291 inhibits the electrode reaction in the blocked area, which causes the active material there to exhibit  
292 hysteresis. This condition leads to an increase in the abnormal potential during the rest period. The  
293 anode of Cell B is partially blocked by the RE during discharge, when a solid-phase concentration  
294 gradient is established along the y-axis. The gradient accumulates during the discharging/charging  
295 process and diminishes during the subsequent rest period.

296 The overall current density at the anode is zero during rest, which means that the local current  
297 density is small. Thus, the local anode potential is described by:

$$\phi_s - \phi_e \approx U_{\text{eq}} \left( \frac{c_{s,\text{surf}}}{c_{s,\text{max}}} \right) \quad (10)$$

298 Lithium diffusion from the blocked to the unblocked area produces a continual decrease in the  
299 solid-phase concentration in the blocked area leading to an increase in the equilibrium voltage,  $U_{\text{eq}}$ .  
300 The measured anode potential,  $V_a$ , increases with increasing  $U_{\text{eq}}$ , which is the origin of the  
301 abnormal feature. The 2D model replicates this process in good agreement with experimental  
302 results as shown in Fig. 5 and Fig. 6. The cell parameters used in the simulation are listed in [Table](#)  
303 [1](#). The different increases in anode potential observed for different final states of charge also are  
304 explained by this model. The differential curve of graphite is shown in Fig. 9. The slope is greater  
305 at low SOC than at high SOC, which indicates that the shift in  $U_{\text{eq}}$  is greater at constant lithium  
306 diffusion.

### 307 **3.4 Parameter influence:**

308 The parameters established for electrode potential measurements significantly influence their

309 accuracy, especially under dynamic CC charging or discharging conditions. The accuracy of the  
310 electrode potential data cannot be established simply by comparing the terminal voltage to the  
311 difference between the anode and cathode potentials. Thus, three different widths, thicknesses, and  
312 current rates were considered to examine their impact on the errors caused by the blocking effect.  
313 An overview of the parameters selected is given in [Table 2](#). The minimum width of the RE is 25  
314  $\mu\text{m}$ , which is on the order of the diameter of the attached Cu wire. The maximum width is similar  
315 to the width of the Ni-Li RE.

### 316 **3.4.1 Width:**

317 To evaluate the effect of RE width on the measurement, a CC charge simulation was carried out  
318 for widths of 25, 300, and 800  $\mu\text{m}$ . The simulation involves a CC charge starting from 0.8 SOC to  
319 an upper cut-off voltage of 4.2 V followed by 1800 s rest period. The average solid-phase  
320 concentration and electrode potential are represented in Fig. 10. To obtain a more explicit  
321 comparison, we generated a normalized concentration by removing the absolute change in solid  
322 concentration to show relative differences along the y- and x-axis coordinates at the  
323 electrode/separator interface.

324 Maxima in the normalized concentration profiles can be explained by the blocking effect of the  
325 RE. Greater RE widths correspond to more significant peaks in the concentration differences as  
326 shown in Fig. 10 (a) and (c). At the cathode, solid concentrations in the blocked area are greater  
327 than in the unblocked area, and the maximum concentration differences are 35, 1514, 3556  
328  $\text{mol}/\text{m}^3$  at widths of 25, 300, and 800  $\mu\text{m}$ , respectively. The area affected by blocking increases  
329 with increasing width. Fig. 10 (b) shows that the measured cathode potential decreases  
330 dramatically below its real value causing an unanticipated measurement error. The error between

331 the measured and real cathode potential is 2, 11, and 27 mV at widths of 25, 300, and 800  $\mu\text{m}$ ,  
332 respectively. The difference in the solid concentration diminishes progressively during the rest  
333 period, as does the error in the measured cathode potential. The solid concentration at the anode is  
334 less in the blocked than in the unblocked area consistent with the hysteresis of intercalation.  
335 Likewise, the measured anode potential is less than its true value, which indicates that lithium  
336 deposition may be overestimated under some conditions during measurement. For example, if a  
337 battery with an 800- $\mu\text{m}$ -wide RE is charged from 0.8 SOC at 1/3 C, experimental data indicate  
338 that lithium deposition will occur within 1380 s as the measured anode potential reaches 0 V vs  
339  $\text{Li}/\text{Li}^+$ , not as shown in Fig. 10 (d).

### 340 **3.4.2 Thickness**

341 Fig. 11 shows the cathode and anode potentials at various RE thicknesses using the same charging  
342 protocol as in section 3.4.1. The measured potential is less than the anticipated value for both the  
343 cathode and the anode at each thickness. When the RE thickness is 5  $\mu\text{m}$ , the average maximum  
344 error of the anode and cathode potentials is 8 mV. The maximum error increases only by 4 and 7  
345 mV at thicknesses of 20 and 100  $\mu\text{m}$ , respectively. Thus, thickness has a less significant influence  
346 than width, which is the more important factor to be considered. **Please note that there is a gap**  
347 **between the positive and negative electrodes where the RE is inserted, leading to deformation of**  
348 **the electrodes. Little difference of the positive and negative electrode potentials is seen between**  
349 **the gap is considered or not in simulation. For this reason, the deviation caused by gap is**  
350 **neglected for brevity. The deviation may become larger for larger width.**

### 351 **3.4.3 C-rate**

352 Although the C-rate is not a RE parameter, its impact should be assessed. A greater C-rate generally  
353 requires a smaller RE. Fig. 12 shows the results of electrode potential measurements with and  
354 without a RE. The average maximum errors of the anode and cathode potentials become negligible

355 at small C-rates as shown in Fig. 12. Thus, the electrode potential data are close to anticipated values  
356 under thermodynamic or quasi-equilibrium conditions, such as during EIS measurements or low  
357 C-rate tests. However, the average maximum errors of the anode and cathode potentials become 11  
358 and 37 mV when the C-rate increases to 1/3 and 1 C, respectively. Therefore, data obtained from  
359 dynamic tests at high C-rates must be scrutinized carefully to ensure their validity.  
360

361 **Table 3** summarizes the average errors of measured electrode potentials produced by simulation  
362 with different charging and discharging parameters. At widths of 25 and 300  $\mu\text{m}$ , the average error  
363 is less than 15 mV under all conditions, which is an acceptable value. However, the average error  
364 at 800  $\mu\text{m}$  increases to 76.5 mV during discharge, which invalidates these experimental data.  
365 Thickness dependent errors are less than 15 mV in all cases except at a 100  $\mu\text{m}$  thickness during  
366 discharge. Average electrode potential errors during charging and discharging are relatively  
367 consistent at all C-rates. Errors are less than 15 mV at C-rates below 1/3 C, although the error  
368 exceeds 15 mV at 1 C. The foregoing results provide important principles for proper application of  
369 REs. Our findings suggest that a conductive, mesh-like material with a proper proportion of  
370 skeleton and pores is an ideal RE substrate that is capable of reducing the blocking effect while  
371 loading enough lithium for long-term use. The performance of a RE with this design is being  
372 investigated by our group.

#### 373 **4. Conclusions**

374 **A new RE design with improved stability and lifetime is proposed for use in lithium-ion batteries.**  
375 **The proposed Ni-Li composite RE can load more lithium than traditional Cu-wire-Li REs. In**  
376 **addition, the molten lithium infusion technique strengthens the attachment between the Ni**  
377 **substrate and lithium metal and prolongs RE lifetime. More insights into battery behavior can be**  
378 **obtained by use of a Ni-Li composite reference electrode of appropriate size.** The impact of Ni-Li  
379 RE dimensions on electrode potential measurement were investigated in dynamic tests and  
380 evaluated on the basis of experimental results and a 2D electrochemical FEM. Abnormal  
381 deviations in negative/positive electrode potentials were observed in dynamic tests during the rest  
382 period following discharging/charging and were interpreted in terms of blocking by the internal

383 RE. The internal RE physically blocks the surrounding Li-ion flow during charging and  
384 discharging and slows the electrochemical reaction of particles in the blocked area. This behavior  
385 introduces hysteresis and produces errors in electrode potential measurements. The abnormality  
386 arising from the blocked effect is reproduced by the 2D FEM. Characteristic lengths, widths, and  
387 thicknesses of the internal RE were analyzed by the FEM to quantify the errors caused by the  
388 blocking effect. The influence of current rate during dynamic tests also was evaluated. The salient  
389 conclusions of our investigation are as follows:

390 1) An internal RE with a width of less than 0.3 mm is sufficient to ensure an electrode potential  
391 measurement error of less than 15 mV.

392 2) An internal RE with a thickness of less than 0.02 mm is sufficient to ensure an electrode  
393 potential measurement error of less than 15 mV.

394 3) When using a 0.3-mm-wide and 0.02-mm-thick internal RE, an applied current rate equal to or  
395 less than  $1/3$  C will produce an electrode potential measurement error equal to or less than 15 mV.

396 Although specific errors may vary for different battery geometries or electrochemical  
397 characteristics, the method described here is useful in analyzing the blocking effects of an internal  
398 RE.

### 399 **Acknowledgement**

400 This work is supported by the National Natural Science Foundation of China (Grant No.  
401 U1564205), Ministry of Science and Technology of China (Grant No. 2016YES0102200). Authors  
402 also appreciate Prof. He Xiangming, Prof. Ai Xinping and Prof. Huang Jun for their valuable  
403 suggestions and Ampere Technology Limited for the technical support.

404

Table 1 Electrochemical properties and geometry parameters of the model

Parameter	Anode	Separator	Cathode
Thickness $L$ (m)	$52 \times 10^{-6}$	$25 \times 10^{-6}$	$50.6 \times 10^{-6}$
Solid phase conductivity $\sigma_s$ ( $\text{S} \cdot \text{m}^{-1}$ )	$100^{34}$		$100^{34}$
Solid phase porosity $\varepsilon_s$	$0.63^b$		$0.51^b$
Electrolyte phase conductivity $\kappa$ ( $\text{S} \cdot \text{m}^{-1}$ )	$\kappa = 0.0911 + 1.9101 \times 10^{-3} c_e - 1.052 \times 10^{-6} c_e^2 + 0.1554 \times 10^{-9} c_e^3$		
Electrolyte phase porosity $\varepsilon_e$	$0.3^b$	$1^b$	$0.3^b$
Solid diffusion coefficient $D_s$ ( $\text{m}^2 \cdot \text{s}^{-1}$ )	$2.5 \times 10^{-14} (1.5-x)^{3.5}$ <sup>35</sup> where $x = \text{SOC}$		$2 \times 10^{-14}$ <sup>35</sup>
Electrolyte diffusion coefficient $D_e$ ( $\text{m}^2 \cdot \text{s}^{-1}$ )	$1.5 \times 10^{-10}$ <sup>35</sup>		
Particle radius $R_s$ (m)	$2 \times 10^{-6}$ <sup>36</sup>		$3 \times 10^{-6}$ <sup>a</sup>
Charge transfer coefficient $\alpha$	$0.5$ <sup>36</sup>		$0.5$ <sup>36</sup>
SEI film resistance $R_{\text{SEI}}$ ( $\Omega \cdot \text{m}^2$ )	$0.01$ <sup>36</sup>		$0$ <sup>36</sup>
Reaction rate $k$ ( $\text{m} \cdot \text{s}^{-1}$ )	$8 \times 10^{-12}$ <sup>a</sup>		$5.3 \times 10^{-12}$ <sup>a</sup>
maximum theoretical concentration $c_{s,\text{max}}$ ( $\text{mol} \cdot \text{m}^{-3}$ )	$31363$ <sup>37</sup>		$51385$ <sup>37</sup>
Faraday constant $F$ ( $\text{C} \cdot \text{mol}^{-1}$ )	$96485$		
Transference number $t_+^0$	$0.363$ <sup>a</sup>		
Initial electrolyte concentration $c_{e,0}$ ( $\text{mol} \cdot \text{m}^{-3}$ )	$1200$ <sup>a</sup>	$1200$ <sup>a</sup>	$1200$ <sup>a</sup>

406

<sup>a</sup> Assumed.

407

<sup>b</sup> Fitted.

408

409  
410

Table 2 An overview of the parameter sets applied in simulation for evaluation of the deviation caused  
by RE

Parameters	Width / $\mu\text{m}$	Thickness / $\mu\text{m}$	C-rate / C
Width	25	20	1/3
	300	20	1/3
	800	20	1/3
Thickness	300	5	1/3
	300	20	1/3
	300	100	1/3
C-rate	300	20	1/20
	300	20	1/3
	300	20	1

411  
412

413 **Table 3 An overview of the deviation caused by RE using different widths, thicknesses and C-rates**

Errors / mV		Width / $\mu\text{m}$			Thickness / $\mu\text{m}$			C-rate / C		
		25	300	800	5	20	100	1/20	1/3	1
CHA	Neg	0.6	6.4	26.6	4.7	6.4	9.5	0.8	6	21.1
	Pos	1.1	5.9	16.2	4.4	5.9	6.6	0.7	5.5	18.8
	Average	0.85	6.15	21.4	4.55	6.15	8.05	0.75	5.75	19.95
DCH	Neg	0.3	10.3	54.5	6.7	10.3	13.3	1.2	7.7	22.2
	Pos	6.2	12.5	98.5	11.9	12.5	35.8	1.3	8.1	24.5
	Average	3.25	11.4	76.5	9.3	11.4	24.55	1.25	7.9	23.35

414

415

416 Fig. 1 Schematic illustration of the RE set-ups used in this study: (a) Cu-wire-Li RE, (b) Ni-Li  
417 composite RE.

418 Fig. 2 Schematic illustration of the 2D model geometry: 3D view (left) and cross section (right) with  
419 a inserted Ni-Li composite RE (white rectangle area) between the electrodes of the cell sandwich.  
420 The 2D model is constructed on the cross section.

421 Fig. 3 Cathode (blue solid line) and anode (green solid line) potentials in the cells with (a) the RE of  
422 Set-up A and (b) the RE of Set-up B during the C-rate tests. Zoomed views of the potentials during  
423 the rest period are shown to highlight the abnormal relaxation potential.

424 Fig. 4 A comparison of the anode/cathode potential profile during the rest period following a  
425 discharge/charge : (a) a normal profile, (b) an abnormal profile.

426 Fig. 5 A comparison between the experimental data and model prediction for (a) cell voltage and (b)  
427 anode potential in the cell with the RE of Set-up B, during a discharge to 0 SOC, followed by a 1 h  
428 rest period.

429 Fig. 6 A comparison between the experimental data and model prediction for (a) cell voltage and (b)  
430 anode potential in the cell with the RE of Set-up B, during a discharge to 0.2 SOC, followed by a 3  
431 h rest period.

432 Fig. 7 Evolution of distribution for the electrolyte concentration at the adjacent region to the RE  
433 during a 3200s discharge at 0.5 C rate, followed by a 1800 s rest period.

434 Fig. 8 Evolution of distribution for the average solid phase concentration at the adjacent region to  
435 the RE during the same 3200s discharge at 0.5 C rate and the following 1800 s rest period in Fig. 7.

436 Fig. 9 Equilibrium potential of the graphite anode (top) and its differential potential (bottom).

437 Fig.10 (a) Debiased average solid concentration along y-axis at the cathode/separator interface, (b)  
438 cathode potential, (c) debiased average solid concentraon along y-axis at the anode/separator  
439 interface, and (d) anode potential during a CC charge at 1/3 C to 4.2 V and a following 1800 s rest  
440 period for different widths of the RE.

441 Fig. 11 (a) Cathode potential and (b) anode potential during a CC charge at 1/3 C to 4.2 V and a  
442 following 1800 s rest period for different thicknesses of the RE.

443 Fig. 12 A comparison for the deviation caused by the RE at various C-rates. (a) Cathode potential  
444 and (b) anode potential during a 1000 s CC charge at different C-rates from 0.5 SOC, followed by a  
445 1000 s rest period.

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448 **Reference**

- 449 1. L. Lu, X. Han, J. Li, J. Hua and M. Ouyang, *J. Power Sources*, **226**, 272 (2013).  
450 2. B. Scrosati and J. Garche, *J. Power Sources*, **195**, 2419 (2010).  
451 3. A. N. Jansen, D. W. Dees, D. P. Abraham, K. Amine and G. L. Henriksen, *J. Power Sources*, **174**,  
452 373 (2007).  
453 4. P. Liu, J. Wang, J. Hicks-Garner, E. Sherman, S. Soukiazian, M. Verbrugge, H. Tataria, J. Musser  
454 and P. Finamore, *J. Electrochem. Soc.*, **157**, A499 (2010).  
455 5. C. Huang, S. Zhuang and F. Tu, *J. Electrochem. Soc.*, **160**, A376 (2012).  
456 6. J. L. Gómez-Cámer and P. Novák, *Electrochem. Commun.*, **34**, 208 (2013).  
457 7. J. R. Belt, D. M. Bernardi and V. Utgikar, *J. Electrochem. Soc.*, **161**, A1116 (2014).  
458 8. J. Costard, M. Ender, M. Weiss and E. Ivers-Tiffée, *J. Electrochem. Soc.*, **164**, A80 (2017).  
459 9. T. Waldmann, B.-I. Hogg, M. Kasper, S. Grolleau, C. G. Couceiro, K. Trad, B. P. Matadi and M.  
460 Wohlfahrt-Mehrens, *J. Electrochem. Soc.*, **163**, A1232 (2016).  
461 10. X. Feng, X. He, L. Lu and M. Ouyang, *J. Electrochem. Soc.*, **165**, A155 (2018).  
462 11. T. Waldmann, M. Kasper and M. Wohlfahrt-Mehrens, *Electrochim. Acta*, **178**, 525 (2015).  
463 12. M. Itagaki, K. Honda, Y. Hoshi and I. Shitanda, *J. Electroanal. Chem.*, **737**, 78 (2015).  
464 13. E. Barsoukov, J. H. Kim, J. H. Kim, C. O. Yoon and H. Lee, *Solid State Ionics*, **116**, 249 (1999).  
465 14. F. La Mantia, C. D. Wessells, H. D. Deshazer and Y. Cui, *Electrochem. Commun.*, **31**, 141 (2013).  
466 15. D. P. Abraham, S. D. Poppen, A. N. Jansen, J. Liu and D. W. Dees, *Electrochim. Acta*, **49**, 4763  
467 (2004).  
468 16. M. Klett, J. A. Gilbert, S. E. Trask, B. J. Polzin, A. N. Jansen, D. W. Dees and D. P. Abraham, *J.*  
469 *Electrochem. Soc.*, **163**, A875 (2016).  
470 17. H. Nara, D. Mukoyama, T. Yokoshima, T. Momma and T. Osaka, *J. Electrochem. Soc.*, **163**, A434  
471 (2015).  
472 18. K. Mitsuda, S. Hara and D. Takemura, *Electrochemistry*, **84**, 861 (2016).  
473 19. D. W. Dees, A. N. Jansen and D. P. Abraham, *J. Power Sources*, **174**, 1001 (2007).  
474 20. M. Ender, A. Weber and I.-T. Ellen, *J. Electrochem. Soc.*, **159**, A128 (2011).  
475 21. S. Klink, E. Madej, E. Ventosa, A. Lindner, W. Schuhmann and F. La Mantia, *Electrochem.*  
476 *Commun.*, **22**, 120 (2012).  
477 22. C. Delacourt, P. L. Ridgway, V. Srinivasan and V. Battaglia, *J. Electrochem. Soc.*, **161**, A1253  
478 (2014).  
479 23. Y. Hoshi, Y. Narita, K. Honda, T. Ohtaki, I. Shitanda and M. Itagaki, *J. Power Sources*, **288**, 168  
480 (2015).  
481 24. M. Ender, J. Illig and E. Ivers-Tiffée, *J. Electrochem. Soc.*, **164**, A71 (2017).  
482 25. Z. Chu, X. Feng, L. Lu, J. Li, X. Han and M. Ouyang, *Appl. Energ.*, **204**, 1240 (2017).  
483 26. M. Dubarry, C. Truchot, M. Cugnet, B. Y. Liaw, K. Gering, S. Sazhin, D. Jamison and C.  
484 Michelbacher, *J. Power Sources*, **196**, 10328 (2011).  
485 27. M. Dubarry, C. Truchot and B. Y. Liaw, *J. Power Sources*, **258**, 408 (2014).  
486 28. J. Zhou and P. H. L. Notten, *J. Electrochem. Soc.*, **151**, A2173 (2004).  
487 29. Y. Liu, D. Lin, Z. Liang, J. Zhao, K. Yan and Y. Cui, *Nat Commun*, **7**, 10992 (2016).  
488 30. S.-S. Chi, Y. Liu, W.-L. Song, L.-Z. Fan and Q. Zhang, *Adv. Funct. Mater.*, **27**, 1700348 (2017).  
489 31. M. Doyle, T. F. Fuller and J. Newman, *J. Electrochem. Soc.*, **140**, 1526 (1993).  
490 32. X. B. Cheng, R. Zhang, C. Z. Zhao, F. Wei, J. G. Zhang and Q. Zhang, *Advanced Science*, **3**

- 491 (2016).
- 492 33. Z. Wang, Z. Li, J. Huang and J. Zhang, *ECS Transactions*, **75**, 151 (2017).
- 493 34. M. Doyle and J. Newman, *J. Power Sources*, **54**, 46 (1995).
- 494 35. W. Fang, O. J. Kwon and C. Y. Wang, *International journal of energy research*, **34**, 107 (2010).
- 495 36. S. Santhanagopalan, Q. Guo, P. Ramadass and R. E. White, *J. Power Sources*, **156**, 620 (2006).
- 496 37. S. Tippmann, D. Walper, L. Balboa, B. Spier and W. G. Bessler, *J. Power Sources*, **252**, 305
- 497 (2014).
- 498